

Creep Behavior of Poly(*N*-isopropylacrylamide) Gels in the Collapsed State

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(Received April 7, 2006; Accepted June 29, 2006; Published August 11, 2006)

ABSTRACT: Creep behavior of cylindrical poly(*N*-isopropylacrylamide) hydrogels in the collapsed state has been investigated. When an elongational stress is applied to the collapsed gels in water, the length of the gels increases and the diameter decreases toward the new equilibrium values. When the stress is removed, the gel recovers the original state through the reverse process. The creep behavior of the collapsed gels is in contrast to the prominent further swelling behavior (*i.e.*, increase in both length and diameter) of the same gels in the swollen state under a constant stress. The similar measurements under constant strains reveal that the collapsed gels undergo a small but definite stress-induced increase in volume. Under sinusoidal stress, the amplitude of the displacement decreases and the phase lag increases as angular frequency increases. The static data agree with the static response estimated from the dynamic data. [doi:10.1295/polymj.PJ2006006]

KEY WORDS Poly(*N*-isopropylacrylamide) Gel / Collapsed State / Creep / Static and Dynamic Stress / Magnetic Force /

Synthesis, properties and functions of polymer gels have recently been investigated by many researchers. A polymer gel consists of a polymer network swollen by a large amount of solvent and has been paid much attention as a unique soft material. The volume of polymer gels varies in response to the change in the environmental factors such as temperature, pH, composition of the solvent.^{1–4} By using these properties or functions, polymer gels have been expected as smart devices in various fields: for example, drug delivery systems and actuators. Poly(*N*-isopropylacrylamide) (PNIPA) hydrogels undergo the volume phase transition in response to an infinitesimal change in temperature, and the transition temperature (T_t) has been reported to be $T_t \approx 32^\circ\text{C}$: A slight increase in temperature causes a drastic decrease in volume around 32°C . Below T_t the gels are highly swollen by water and this state is called “swollen state”. Above T_t the gels consist of polymer network and a very small amount of water, which is called “collapsed gels”, or “gels in the collapsed state”. In the previous papers^{5,6} we reported the swelling behavior of the PNIPA hydrogels in the swollen state below T_t under static or dynamic stress. Elongational stress applied to the fully swollen gels induces a further swelling as a result of the shift to another equilibrium state under deformation. This phenomenon is called “stress-induced swelling” and has become of much interest.^{6–8} By contrast, there are few corresponding measurements on the PNIPA gels in the collapsed state above T_t and thus the details of the deformation behavior of the collapsed gels are still unclear.^{9–11} In

the present paper, we report the creep behavior of the collapsed PNIPA gels under static and dynamic stresses (or strains) revealed by the same method in the previous papers.^{5,6}

EXPERIMENTAL

Preparation of Gel Samples

Poly(*N*-isopropylacrylamide) (PNIPA) hydrogels were synthesized by radical copolymerization of *N*-isopropylacrylamide (NIPA) and *N,N'*-methylenebis(acrylamide) (BIS). First, *N*-isopropylacrylamide and BIS (as a crosslinker) were dissolved in distilled water under nitrogen atmosphere. The total monomer concentration of NIPA and BIS was fixed to be 6 wt %, and the molar ratio [NIPA]/[BIS] was also fixed to be 100. After ammonium peroxodisulfate (initiator) and *N,N,N',N'*-tetramethylethylenediamine (accelerator) were added into the system, the pregel solution was transferred into cylindrical glass capillaries and the gelation was performed at 5°C for 24 h. The cylindrical gel samples were then removed from the capillaries and were poured into a large amount of methanol at room temperature to exchange the solvent from water to methanol. The methanol outside the gels was exchanged at several times. The gels swollen by methanol were dried *in vacuo*, and then after they were soaked in water at about 50°C to obtain the samples in the equilibrium collapsed state. The dimensions of the samples used for mechanical tests were 10–20 mm in length and 0.5–2.0 mm in diameter.

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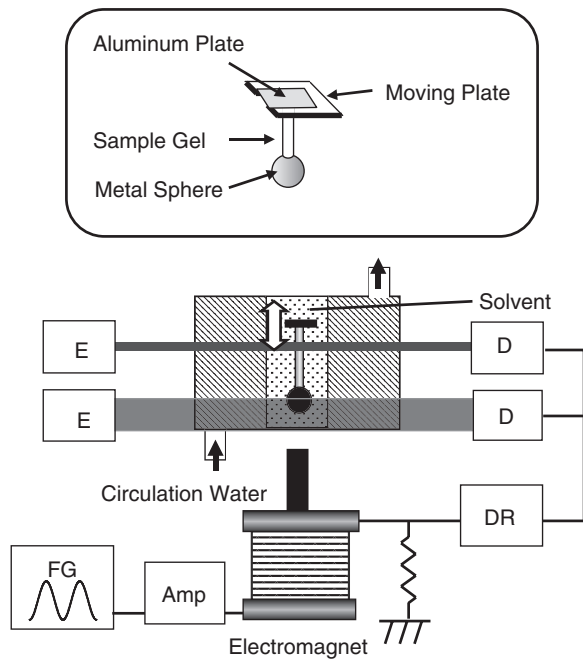


Figure 1. The schematic representation of the magnetic force-driven rheometer. FG; function generator; Amp; power amplifier; E; emitter part of laser scan micrometer; D; detector of laser scan micrometer; DR; Digital Recorder.

Apparatus

A laboratory-made magnetic force-driven rheometer was used to investigate the static and dynamic extensional properties of the PNIPA hydrogels in the collapsed state. Figure 1 shows the schematic representation of the rheometer built up originally in the previous study.^{5,6} One end of the cylindrical gel was pasted to a metal (tungsten carbide) sphere and the other end to an aluminum plate using a cyanoacrylate-type adhesive. The aluminum plate with a gel sample was mounted on a moving plate and the system was set in a double-jacketed solvent bath. The surrounding solvent of the fully swollen gel was water. Temperature-controlled water was circulated in the outer bath to keep the solvent of the inner bath to be a constant temperature (at $\sim 40^\circ\text{C}$) throughout this study.

In stress-controlled operations, magnetic force was imposed to the metal sphere by applying the amplified current to the coil. The current was obtained by the combination of a NF power amplifier (4010 High Speed Power Amplifier/Bipolar Power Supply) and a Yokogawa function generator (FG200). Static stresses acting on the gels were generated by DC, the dynamic stress originating from AC. The dimension of the gels was measured as a function of time (t) by two sets of emitter-detector units (Laser Scan Micrometer; Keyence, LS5500): One monitored the diameter and the other the position of the metal sphere from the bottom of the bath (from which the length of the gels

is estimated). The wave-form data from the output of the detectors were memorized with a Yokogawa analyzing recorder (AR1100A) together with the wave-form data of the current in the coil. Details of the experimental conditions are the same as the previous paper.^{5,6}

In strain-controlled operations, one end of the gels was settled with a larger, hence heavier, metal sphere; in this condition, the gel is elongated by about 50%, and the metal sphere touches on the bottom of the bath. As a result, the strain in the stretching direction is fixed throughout the measurement. The length of the gels was fixed to be a constant value and was estimated by the height of the moving plate from the bottom, while the change in diameter was determined by using a set of emitter-detector unit. In this operation, liquid paraffin (LP) as well as water (W) was employed as the surrounding solvent of the fully swollen gel by water. LP is a non-solvent for PNIPA.

RESULTS AND DISCUSSION

Static Properties

In the static measurements, the total static stress was composed of the two components: the stresses induced by weight and magnetic force. Correspondingly the two contributions of strain can be defined.

$$\sigma_S = \sigma_W + \sigma_M \quad (1)$$

$$\varepsilon_S = \varepsilon_W + \varepsilon_M \quad (2)$$

Eq 1 is the relation for stress and eq 2 for strain. The subscripts, S, W and M mean the (total) static, weight and magnetic, respectively. For the length in the static measurements l_S , we have

$$l_S = (l_0 + l_W) + l_M \quad (3)$$

corresponding to eq 2. Here, l_0 is the length without stress. Since the stress σ_W was much smaller than σ_M in all static experiments, $\sigma_S \approx \sigma_M$ and then $\varepsilon_S \approx \varepsilon_M$ were assumed, and a quantity l_i was used as an initial length instead of l_0 when strains were calculated. The lengths l_i and l_0 are related with $l_i = l_0 + l_W$.

Filled symbols in Figure 2 show the t -dependence of the length (l) and diameter (d) after the application of the static stress to the collapsed PNIPA gel in water. In this measurement the maximum strain in the axial direction is *ca.* 3% which is within linear elasticity region. The length l increases (Figure 2a) and the diameter d decreases (Figure 2b) with increasing time, and these reach the equilibrium values at about $t = 600$ s. This behavior is actually a kind of creep, and is substantially different from the behavior of the PNIPA gels in the swollen state: Both length and diameter of the swollen gels increased under a constant stress, namely, the gels in the swollen state

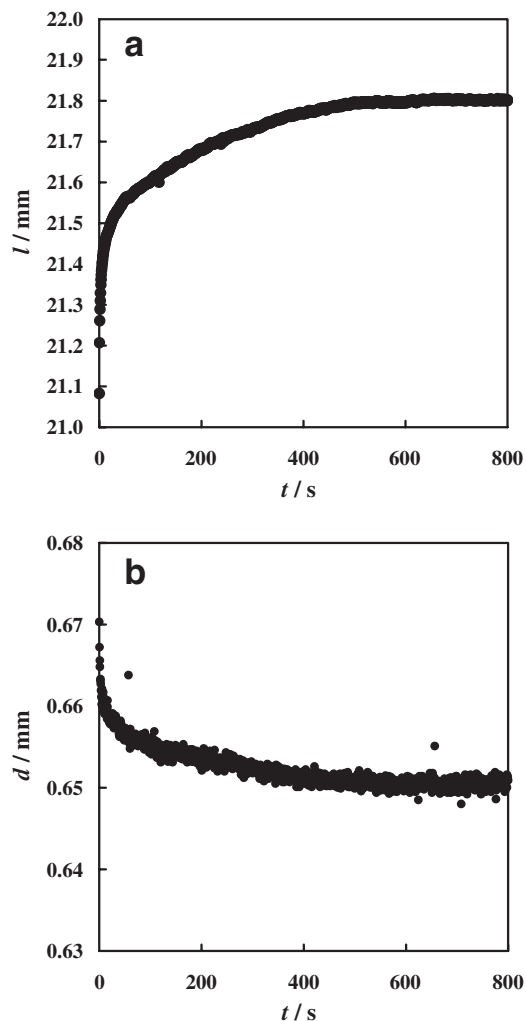


Figure 2. Time dependence of (a) the length (l) and (b) the diameter (d) of the PNIPA hydrogel in the collapsed state after applying the a static stress (the voltage of the applied DC is 4 V).

clearly showed the further swelling induced by the static stress.⁶ The different behavior of the collapsed and swollen PNIPA gels under a constant stress probably results from the difference in cross-links. The collapsed PNIPA gels have the cross-links formed by hydrogen bonds in addition to the cross-links made of covalent bonds owing to the high network density.⁹ The network concentration of the collapsed gel is about eight times as large as that in the swollen state. In contrast the swollen gels were made only of the covalent bonds. When the mechanical stress is applied to the collapsed gel, the hydrogen bonds are destroyed instantaneously by the stress. But all hydrogen bonds are not destroyed at once. Only the hydrogen bonds which directly supports the force are destroyed. In addition, new hydrogen bonds are generated in other places at the same moment because the some network chains come close each other by the deformation. Through the deformation of the gel, the network repeats the generation as well as destruction, namely

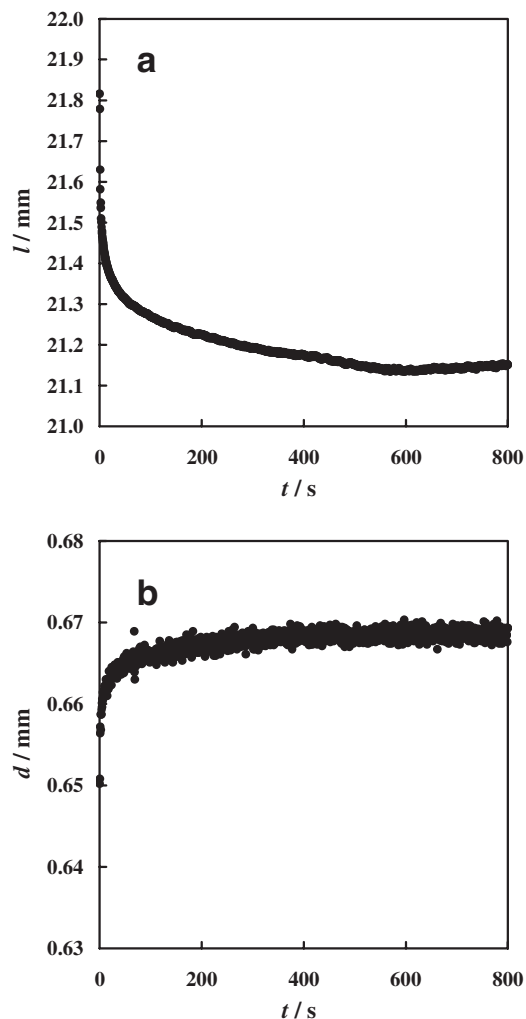


Figure 3. Time course of (a) the length (l) and (b) the diameter (d) of the gel after releasing the applied stress.

the recombination, of the hydrogen bonds. This causes the slow creep behavior of the collapsed gel. When the elastic force of the network balances with the applied stress, the recombination of the hydrogen bonds ceases.

Figure 3 shows the t -dependence of l and d for the collapsed gel in water after the applied stress is removed. The length decreases (Figure 3a) and the diameter increases (Figure 3b) with increasing elapsed time. At about $t = 600$ s the gel reaches the equilibrium state, which is very close to the original state before deformation. This corresponds to the process of creep recovery. After the removal of the applied stress, the creep recovery proceeds *via* the reverse process of the recombination of the hydrogen bonds.

The Figure 4a shows the t -dependence of d after applying the static strain in water. The applied strain is about 50% and the inset shows the result for the small strain of about 5%. The initial diameter before deformation was 2.4 mm. The static strain induces a

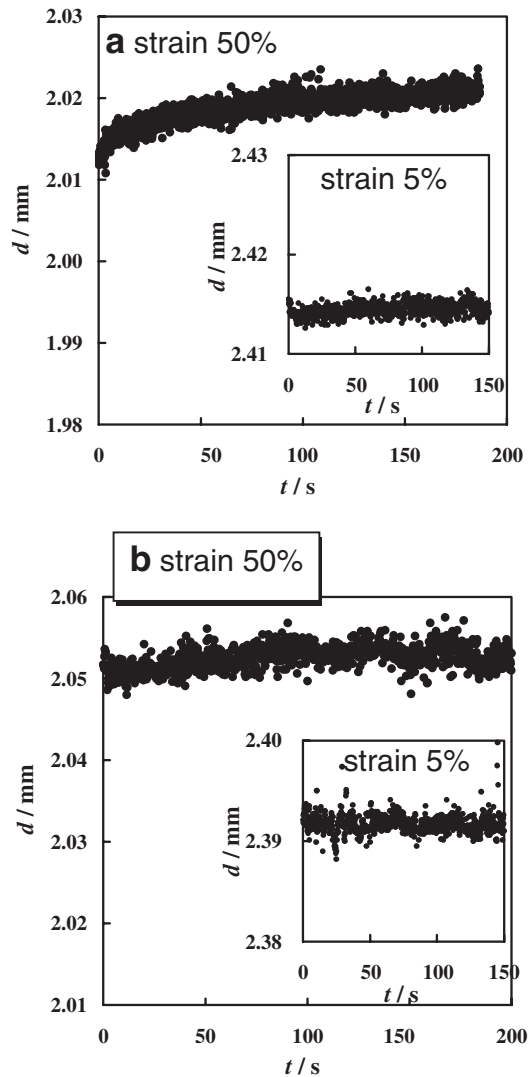


Figure 4. Time dependence of the diameter (d) of gel under 50% strain in (a) water and (b) LP. The each inset is same value of 5% strain.

finite further swelling. The stress-induced swelling^{6–8} becomes more clearly recognizable as the strain increases. In the case of 50% strain, the diameter levels off at about 150 s. The results of the static strain experiments confirm that the stress-induced swelling occurs even in the collapsed state although the magnitude is smaller than that in the swollen state. The stress-induced swelling was not recognizable in the variation of d in the constant stress experiment (Figure 2). This is probably because the increasing in d by the stress-induced swelling is effectively masked by the decrease in d caused by the creep. Figure 4b displays the results of the similar experiments in LP (non-solvent for PNIPA). The diameter of the gel shows no appreciable change over the whole range of t . These results further confirm that the variation of d in water (Figure 4a) are attributed to the stress-induced swelling.

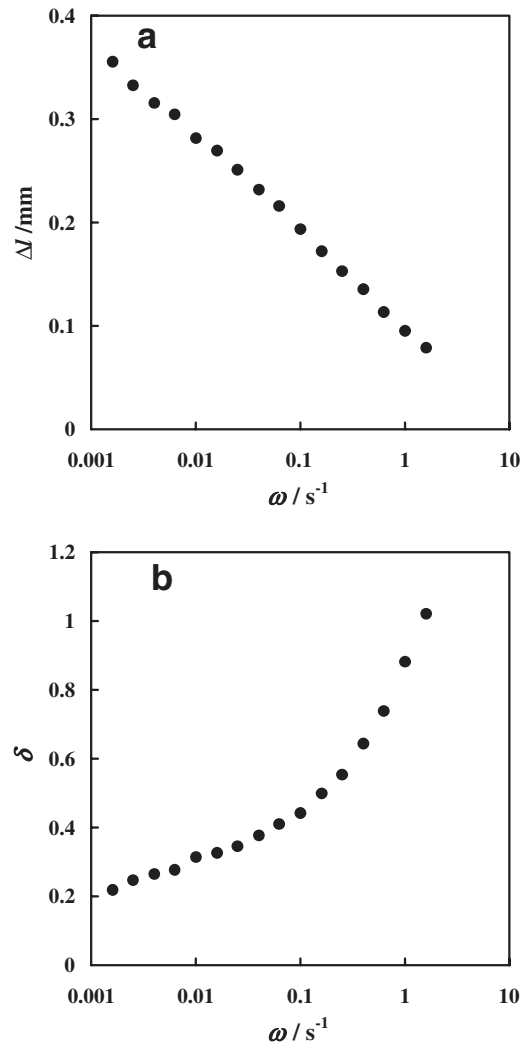


Figure 5. (a) Amplitude of the displacement induced (Δl) by the dynamic stress as a function of angular frequency (ω), and (b) phase lag (δ) determined as a function of angular frequency (ω) (the amplitude of the applied AC voltage is 2 V).

Dynamic Properties

In order to analyze the dynamic data, several quantities should be defined. The dynamic part of the stress (σ_D) is expressed by

$$\sigma_D = \sigma_0 \sin(\omega t) \quad (4)$$

Here σ_0 and ω represent the amplitude of the dynamic stress and the angular frequency, respectively. We redefine the variation of length for the gel in the dynamic measurements (l_D) as

$$l_D = \Delta l \sin(\omega t - \delta) \quad (5)$$

Here Δl , and δ represent the amplitude of the displacement and the phase lag (measured from the stress), respectively.

Figure 5 shows the semi-logarithmic plots of Δl and δ against ω for the PNIPA hydrogel in the collapsed state. The amplitude Δl decreases monotonically

cally with increasing ω and the value of Δl at the lowest frequency is about five times as large as that at the highest frequency. This is different from the results for the PNIPA gels in the swollen state,⁶ where the two plateau regions emerge in the low and high frequency limit. Figure 5b shows the plots for δ . The phase lag increases with increasing ω , and at high frequencies δ increases very steeply. This behavior is also different from that in the swollen state.⁶ To analyze the dynamic data in Figure 5, it is useful to decompose Δl into two parts: the in-phase part ($\Delta l'$) and the out-of-phase part ($\Delta l''$). Each can be written by

$$\Delta l' = \Delta l \cos \delta \quad (6)$$

$$\Delta l'' = \Delta l \sin \delta \quad (7)$$

Figure 6 shows the ω -dependence of $\Delta l'$ and $\Delta l''$ (circles and squares, respectively) of the PNIPA gel. The in-phase part $\Delta l'$ decreases with increasing ω as in the case of the Δl , whereas $\Delta l''$ is almost constant over a wide range of ω . This indicates that the creep occurred with the same intensity in the whole ω -range examined because $\Delta l''$ corresponds to the creep intensity.

Comparison between Static and Dynamic Data

In order to check the consistency between the static and dynamic data of the collapsed gels, we compare the experimental data obtained from static measurements with the static response calculated from the dynamic data. The gel specimen is the same for the static and dynamic tests (Figures 2 and 6, respectively). On basis of the almost ω -independent $\Delta l''$, we assume the following spectrum.

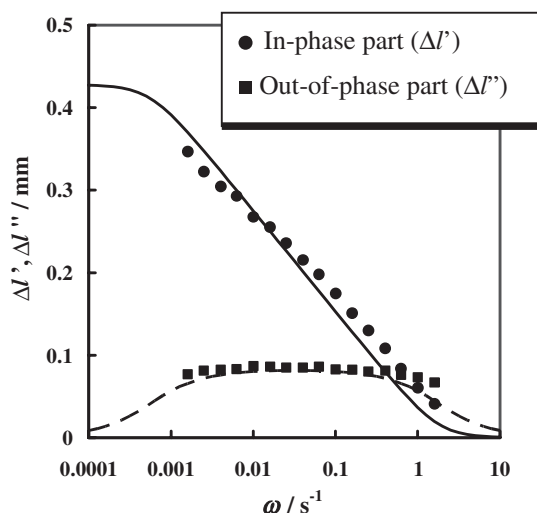


Figure 6. In-phase part ($\Delta l'$; ●) and out-of-phase part ($\Delta l''$; ■) of the amplitude of the displacement as a function of angular frequency (ω). The best fit curves of $\Delta l'$ and $\Delta l''$ also shown as a solid line and broken line (see text).

$$\Delta l^* = k \sum_{n=1}^m \frac{1}{1 + i\omega\tau_n} \quad (8)$$

where Δl^* is defined by

$$\Delta l^* \equiv \Delta l' - i\Delta l'' \quad (9)$$

The functions $\Delta l'$ and $\Delta l''$ from eq 9 satisfy the Kramers-Kronig relation.¹² The mechanism of the change in length is assumed to be of multi-mode, each being only virtual and not corresponding to the real mode of motion. In eq 8, k and τ_n are respectively the intensity and the retardation time of the n -th mode ($n = 1, 2, \dots, m$). The distribution of τ_n in eq 8 is separated with the same time interval in a logarithmic scale. The cut-off value of τ in the long time limit is assumed as $\tau_1 = 1000$ s. Although the edge in the lower frequency side of the box-shape spectrum was not observed in the dynamic test, but it is simply expected that τ_1 is not so far from the longest retardation time (~ 200 s) directly obtained in the static experiment. The intensity k ($= 0.061$ mm) and the cut-off value of the short time limit (τ_7) were evaluated by the best fitting with $m = 7$ to the data of $\Delta l'$. The value of m ($m = 7$) is chosen so that eq 8 can reproduce the box-type spectrum, and the values of $m \geq 7$ yield the same results as $m = 7$. The fitting result is shown in Figure 6.

Let $\Delta l(t)$ be $l(t) - l_0$, and we have

$$\begin{aligned} \frac{d}{dt} \Delta l(t) &= \frac{k}{2\pi} \sum_{n=1}^7 \int_{-\infty}^{\infty} \frac{1}{1 + i\omega\tau_n} \exp(i\omega t) d\omega \\ &= k \sum_{n=1}^7 \frac{1}{\tau_n} \exp\left(-\frac{t}{\tau_n}\right) \end{aligned} \quad (10)$$

Integration of the above equation over t with the initial condition for $\Delta l(t)$ gives

$$\Delta l(t) = k \sum_{n=1}^7 \left[1 - \exp\left(-\frac{t}{\tau_n}\right) \right] \quad (11)$$

Figure 7 compares the result of the static test (the data in Figure 2a) and the curve calculated from eq 11. The good agreement shows that the dynamic and static data are consistent. The fitted values of the initial length and k are 21.08 mm and 0.11 mm, respectively. This value of k is about twice as large as $k = 0.061$ for the fitting to the dynamic data. This is reasonable because the effective magnitude of the applied stress (voltage) in the static test (Figure 2) is two times larger than that in the dynamic test (Figure 5).

CONCLUSION

We investigated the creep behavior of the cylindrical PNIPA hydrogels in the collapsed state. When a

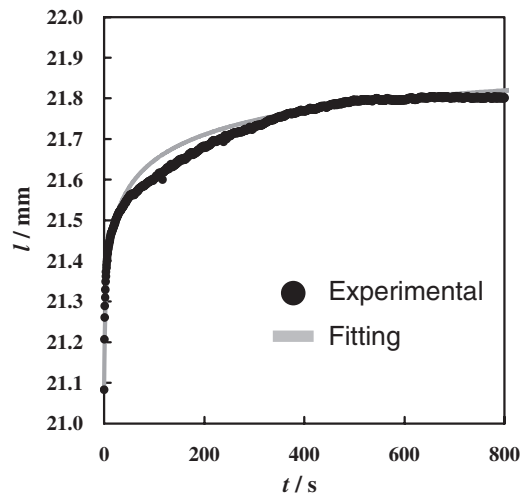


Figure 7. Time dependence of the length (l) (black circle) after applying the a static stress in Figure 2a and the best fit curve converted from dynamic date (gray line).

constant stress was applied to the collapsed PNIPA gels in water, the length of the gels increased and the diameter decreased toward the new equilibrium values. When the stress was released, the length and diameter recovered the original values before deformation. The creep and creep recovery originated from the destruction and generation of the hydrogen bonds in the collapsed gels. In the measurements under constant strains, a small but definite stress-induced swelling occurred.

In the dynamic measurements, the amplitude of the displacement in length decreased and the phase lag

increased as angular frequency increases. The static properties obtained by the conversion of the dynamic data agreed with the static data in the experiment.

Acknowledgment. This research was supported in part by the 21st century COE program “COE for a United Approach to New Materials Science” from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

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